

# **SAMPLING STRATEGIES FOR DETERMINING NUTRIENT LOADS IN STREAMS**

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## **Biographical Sketch of Authors**

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## **Abstract**

Accurate measurements of nutrient and pollution loads in streams are critical for detecting water quality trends, determining the impacts of non point source (NPS) pollution, and developing TMDLs. Much or most of the load in a stream occurs during surface runoff events (storms). For several years, we at the Arkansas Water Resources Center (AWRC) have sampled and calculated nutrient loads for Northwest Arkansas streams in the White and Illinois River watersheds. This paper will summarize our ongoing efforts to find the best sampling methods for our objectives and to address the comparability of different sampling and load calculation methods. We compare simple grab samples, intensive automatic sampling, and spatially integrated composite samples. We will also present the results of a project comparing loads calculated from regression models using sparse data to loads integrated from more frequent data. An ongoing dispute between Arkansas and Oklahoma over phosphorus loading in the Illinois River serves as a good example of the importance of accurate sampling.

## **Introduction**

Determining river water quality is a complex issue and there is no “best” method for sampling. Each method has its advantages and disadvantages. There are essentially three aspects to river water sampling and analysis: 1. gathering data (sampling), 2. calculating loads and/or mean concentrations, and 3. determining trends. Each aspect can be accomplished by several different methods and the aspects are interrelated – the methods chosen for one aspect will influence or be influenced by the methods chosen for another aspect. The sampling protocol must be chosen to provide adequate data to quantify the impacts on the water body. The protocol chosen will depend on the goals of the sampling program, the characteristics of the river, and the characteristics of the suspected source of pollution.

For point sources, the greatest concentrations are during low flow. The variability of the concentration in time and the variability of the concentration in space are relatively simple to characterize. On the other hand, non-point sources produce their highest concentrations at high flows (surface runoff events) and often 50% or more of the loads occur during 5% of the time. During high flow events (storms), concentrations are highly variable, especially in time.

There are essentially two approaches to storm sampling in streams. One is to use an autosampler that can take many samples in time, but is spatially biased. The other is to take one spatially integrated sample at one point in time. These have their advantages and disadvantages and which method is better may depend on whether the spatial or temporal variability is deemed more important and how well the data can be calibrated.

Storm loads can be estimated from limited data using a load calculation model that incorporates the correlation between concentration and flow. However, unless the sampling scheme is planned to capture samples during high-flow events, the sampling data may not contain enough high flow concentration data to confidently make those correlations and the resulting load calculations can be inaccurate and imprecise. “Storm-chasing” to capture a storm event sample or automatic storm sampling using frequent discrete samples or flow-weighted composites can be used to more accurately measure storm loads.

## **Illinois River Sampling**

The Illinois River originates in Arkansas and flows into Oklahoma where it forms the Lake Tenkiller reservoir and then empties into the Arkansas River. The Illinois River in Oklahoma is designated as a scenic river. A dispute between the states over water quality in the Illinois River and how it affected Lake Tenkiller reached the U.S. Supreme Court. The court ruled that downstream state’s water quality laws must be met but that this did not exclude additional discharge from up stream sites. The states established a goal of a forty percent reduction of the 1980-93 total phosphorus load to Lake Tenkiller, and agreed to monitor progress toward that goal by comparing the 1980-93 load to five year moving averages of current data. However, the fact that phosphorus concentrations in the river may now actually be rising and a plan by the city of Fayetteville to build a new wastewater plant and increase its phosphorus loading to the Illinois River has renewed discussion and debate about phosphorus in the Illinois River. Oklahoma is currently (Spring 2002) in the process of adopting an in-stream limit of 0.037 mg/L for phosphorus in scenic rivers – about a tenth of the current level in the Illinois River. At least four entities monitor the Illinois River phosphorus concentrations and it is unclear which data will be used in what way to evaluate progress toward the mutual goal of lower phosphorus in the river.

The Illinois River in Arkansas near the Oklahoma state line is sampled by three different agencies using three different methods for sampling and load determination. The Arkansas Department of Environmental Quality (ADEQ) takes grab samples every other month and calculates loads by averaging concentrations. The U.S. Geological Survey (USGS) takes equal-width-interval (EWI) composite samples 12 times per year and calculates loads using a regression model. AWRC takes grab samples 26 times per year (every 2 weeks) plus flow-weighted

auto-sampler composite samples during all storm events and calculates loads by integration. In addition, Oklahoma performs sampling and analysis on the Illinois River on the Oklahoma side of the border. Figure 1 shows the total phosphorus loads calculated by the three agencies over the past four years. Figure 2 shows the loads calculated by AWRC divided into base and storm loads.

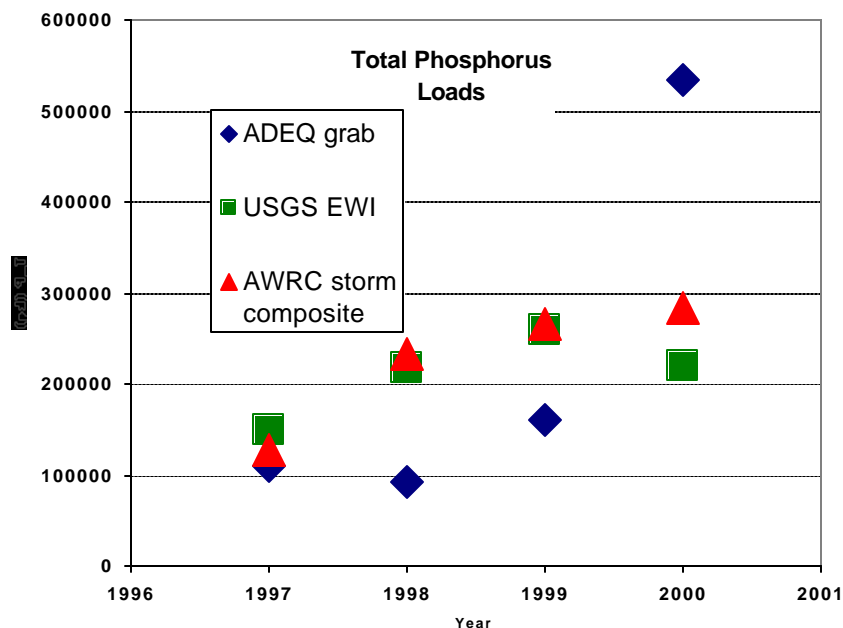


Figure 1 – Total Phosphorus Loads on the Illinois River as Calculated by Three Agencies

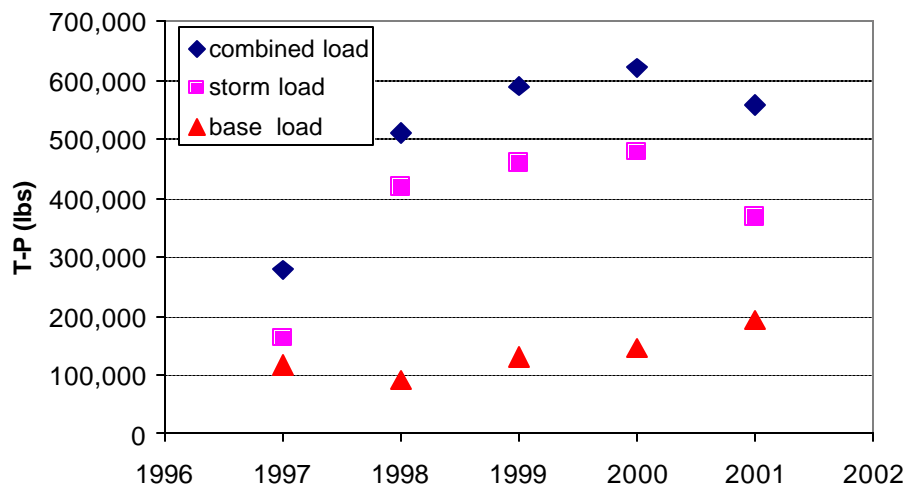


Figure 2. Base, Storm, and Combined Total Phosphorus Loads at the Illinois River

## Comparison of Sampling Methods

Grab samples taken on even time (routine) intervals miss most storm events. Storm flows at the Illinois comprise most of the annual load, but only occur 5% of the time. Therefore, only about 5% of the grab samples are storm samples. Grab samples sample only a single point in space and do not characterize temporal variation. The use of routine grab samples for load determination has two claims to validity: 1. grab samples can characterize base flow and point source loads, and 2. over very long periods of time the impacts of storm flows will eventually be observed. In Figure 1, we see that the ADEQ loads were lower than the other estimates for the first three years, then much higher for the last year. It is probable that during this last year, a grab sample happened to occur during a storm event.

EWI sampling takes a spatially integrated sample during one point in time during a storm. A composite is taken of vertical slices on equal width intervals across the river. The USGS protocol includes routine samples along with some targeted storm samples. Although EWI storm samples are taken at only one point in time during the storm, that point is somewhat random in time and therefore some temporal variability is accounted for in a whole dataset.

Autosamplers sample only one point in the stream cross-section, but can be programmed to sample frequently in time. The AWRC protocol includes routine grab samples along with autosampling of all storms. During the first year of a new AWRC sampling site, autosamplers are typically programmed to take samples every thirty minutes during the rising limb of a hydrograph and every hour during the falling limb. This gives detailed information about the variability of concentration during a storm. In subsequent years, the autosamplers are programmed to take flow-weighted composites during storms. Figure 3 is a schematic showing the difference between EWI and autosampling approaches.

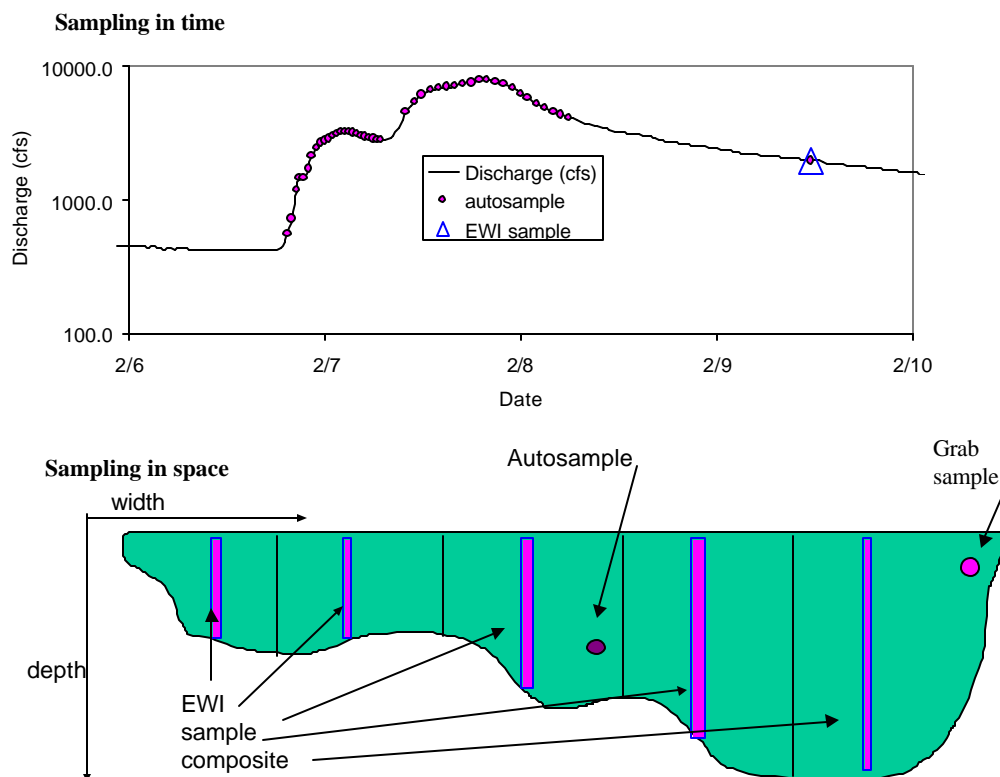


Figure 3. EWI Samples (sampling in space) and Autosamples (sampling in time)

At the Illinois River site and the Kings River site, samples taken by AWRC automatic samplers were compared with those taken concurrently by USGS using the EWI method. At the Kings River site, nine USGS samples were taken concurrently with AWRC automatic samples and analyzed at the AWRC lab. Figure 4 shows a comparison between the samples for phosphorus. We see that there is a strong relationship, although there are differences for some samples. As expected, the differences are greater for total phosphorus, which tends to be more variable with flow and correlated to solids and non point source runoff.

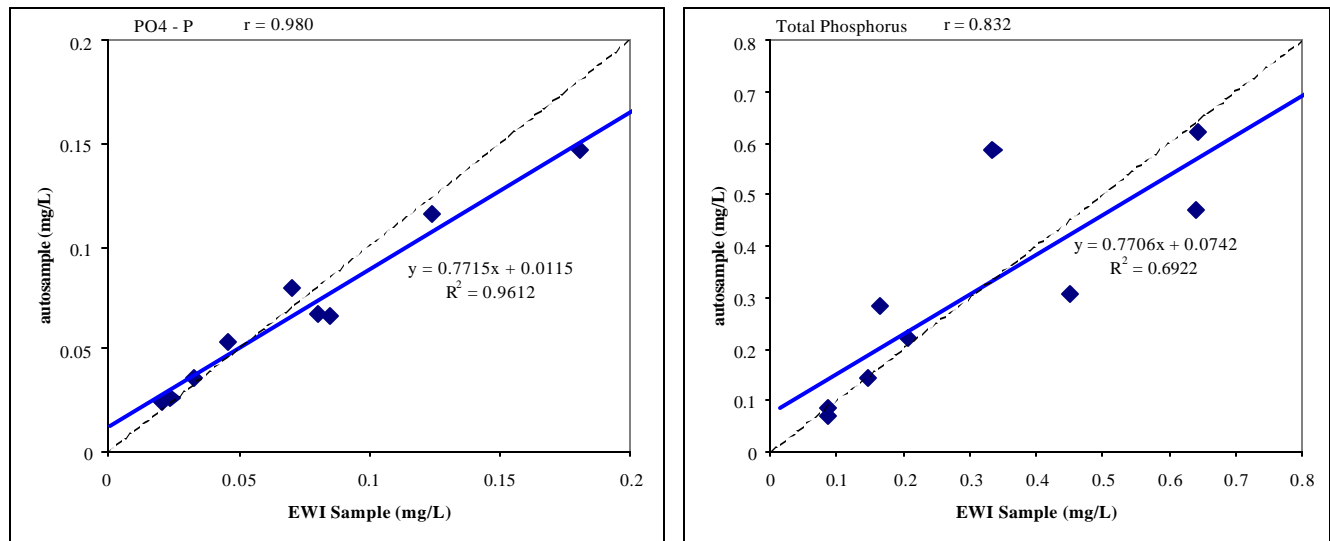


Figure 4 – Autosamples versus EWI samples for (a) Soluble Reactive Phosphorus and (b) Total Phosphorus

### Comparison of Load Calculation Methods

Loads are estimated by multiplying the concentration values by the streamflow volumes for a given time period. Concentrations for time periods that were not sampled can be estimated by the integration method or by the rating curve (regression) method. Using the integration method, constituent concentrations are plotted through time, and missing concentrations are filled in by interpolating between measured concentrations. Integration is accurate when data is abundant, but integrated loads are sensitive to sampling interval. In general, integration of more sparse data tends to underestimate loads because high-flow events are missed. Figure 5 demonstrates this sensitivity, it was produced by taking a dense dataset and calculation loads from every other data point (interval = 2), every third data point (interval = 3), etc... This trend is demonstrated in more detail by Soerens et al. (2000).

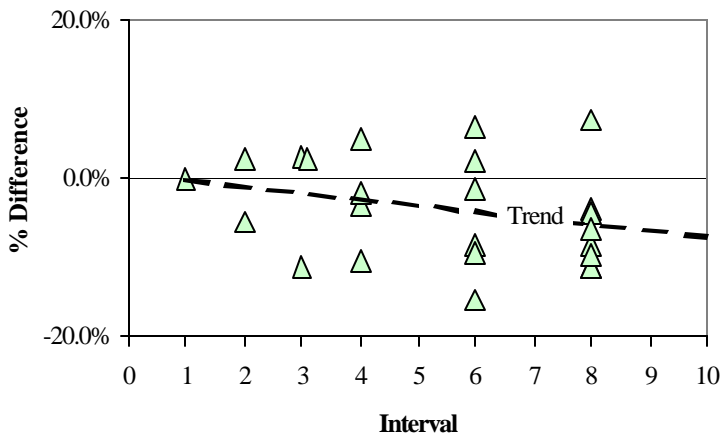


Figure 5. Sensitivity of Integrated Load to Sampling Interval.

The regression method (Cohn, 1995) uses the relation between concentration (or load) and daily average flow to estimate daily concentrations (or loads) of the constituent. The daily loads can then be summed to calculate an annual load. The regression approach has come into widespread use because it requires less data than integration, it can be used to produce estimates for periods beyond when concentration data were collected, and it enables confidence limits to be placed on the estimates as a measure of the modeling error.

The 1998 data from the Illinois River site were used to compare total phosphorus loads calculated by the USGS ESTIMATOR regression model using subsets of the data to loads calculated by integration of the data. Data was subsampled from the entire dataset to simulate various sampling schemes. 20 simulations were run for sampling intervals of 15, 30, 45, and 60 days for each of four cases – no storm samples, 9 storm samples from upper 50% of flow, 9 storm samples from upper 50% with regression on Q only (removes seasonal/time component), and 9 random storm samples. The results are summarized in box plots in Figure 6. In the box plots, the boxes represent the 25<sup>th</sup> to the 75<sup>th</sup> percentiles of the 20 estimates with the middle line being the median, and the whiskers extend to the 10<sup>th</sup> and 90<sup>th</sup> percentiles. We see that the central tendency of the ESTIMATOR loads is accurate when storm data is included, but that annual load estimates can vary. More details can be found in Soerens and Nelson (2001), Green and Haggard (2001), and Haggard, Soerens, and Richards (2002).

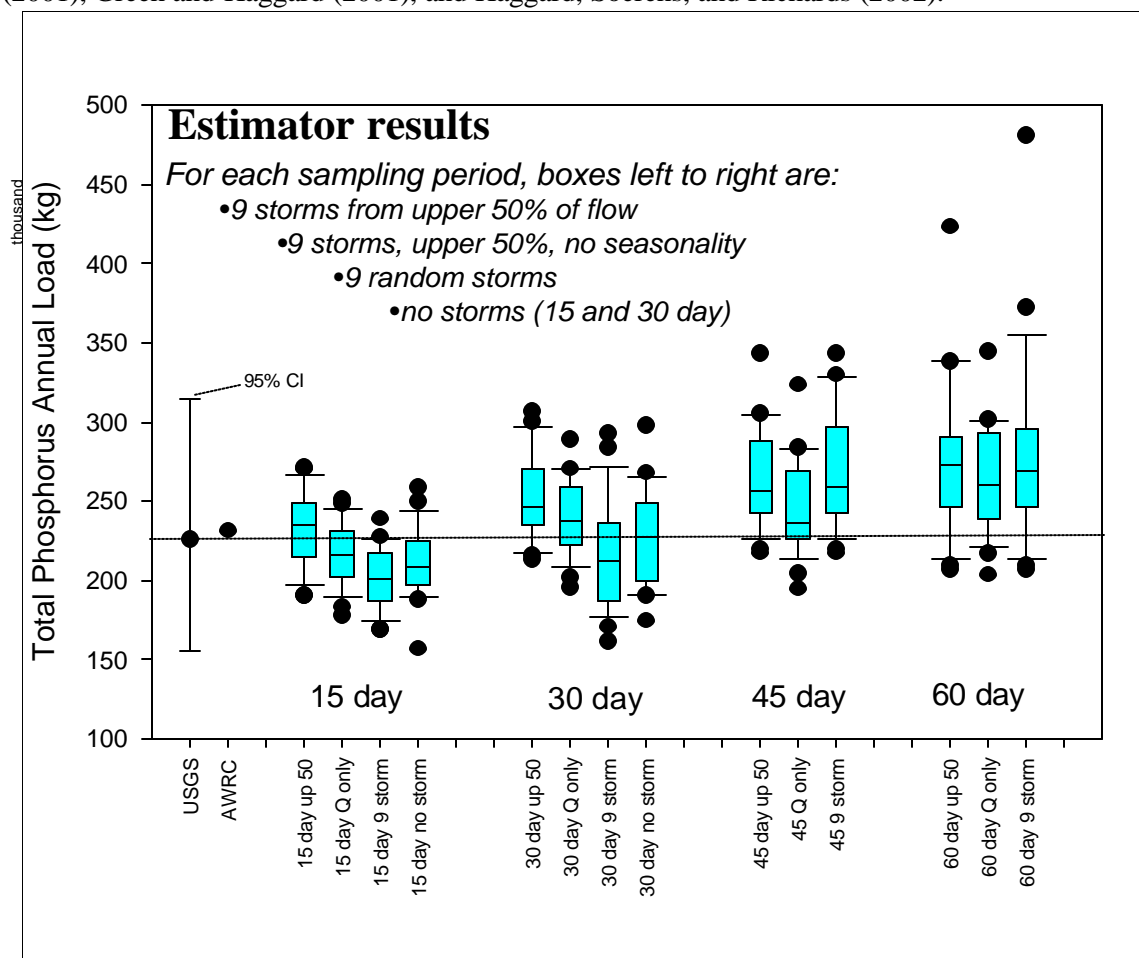


Figure 6. Load Simulation Results

## **Trend Determination**

Often, one of the major goals of a sampling program is to see if the water quality is improving or degrading, i.e., to determine trends. In order to determine trends, an adequate baseline must be developed and criteria for success must be established. A sampling program with less error will enable the detection of trends sooner and the detection of smaller trends. Because concentrations and loads are closely correlated to flow, the hydrological variation must be considered and accounted for in trend detection.

## **Summary and Conclusions**

It is clear that storm sampling is necessary to accurately calculate annual loads of compounds that are present in non-point sources. There are several ways to sample storms and several ways to calculate loads, each method has advantages and disadvantages. The methods used in a sampling program should be chosen based on the goals of the program in terms of accuracy, precision, and trend detection. Frequent sampling and interrelation of variables are both sources of water quality information that should be used in a way to most efficiently and accurately estimate loads. The variability in the natural system and in the methods must be understood to properly interpret sampling results and assess water quality.

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